



PREPARATION OF ALLYL-CONTAINING PDMS TELEHELICS BY THE ANIONIC RING-OPENING POLYMERIZATION

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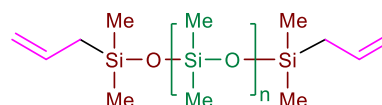
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Abstract

The synthesis of allyl-containing PDMS telechelics from octamethylcyclotetrasiloxane and 1,3-diallyl-1,1,3,3-tetramethyldisiloxane as a stopper by the anionic ring-opening of a siloxane ring is presented. A series of the polymers with the molecular weights from 1000 to 12000 were obtained and characterized by gel permeation chromatography and ¹H NMR spectroscopy. The molecular weights of the resulting polymers correspond to the given ones.

Key words: polysiloxanes, catalytic rearrangement, ring-opening polymerization, polydiorganosiloxane telechelics, allylsiloxanes.



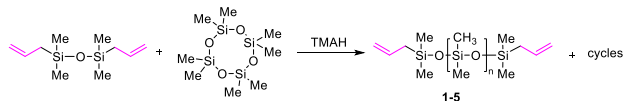
Introduction

Polydimethylsiloxane telechelics (PDMSs) with different organic shells amount to the first products with well-defined structures in this class of high-molecular compounds, used as reagents for the targeted molecular design of siloxane polymers and materials. The method of a siloxane ring opening is one of the first reactions in the polymer chemistry of silicones [1–3].

Herein, the synthesis of allyl-containing PDMS telechelics by the anionic opening of a siloxane ring is presented [4, 5]. The resulting polymers are promising for the production of materials by the hydrosilylation reaction [6, 7]. The advantage of this process is the simplicity of performance and isolation of the target products, which includes the catalyst decomposition at elevated temperatures and evaporation of the volatile products [8]. Earlier it was used for the preparation of only one allyl-containing PDMS [9], but the details of the synthesis were not described in the paper.

Results and discussion

In this work, we demonstrated the synthesis of allyl-containing PDMS telechelics by the mechanism of the anionic opening of a siloxane ring of octamethylcyclotetrasiloxane (D4) in the presence of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane as a chain terminator and tetramethylammonium hydroxide (TMAH) as a catalyst (Scheme 1).



Scheme 1. Synthesis of the allyl-containing PDMSs.

The process was carried out at 100 °C for 5 h until the formation of the maximum content of high-molecular products, which was monitored by gel permeation chromatography (GPC) (see the Electronic supplementary information (ESI)). The calculated and obtained molecular weights of the resulting polymers are presented in Table 1.

The formation of the polymers with terminal allylsilyl groups was confirmed by ¹H NMR spectroscopy (Fig. 1). The presence of the allyl proton signals in the spectra indicated their presence in the polymer. A coincidence of the ratio of the integral intensities of the allyl and methyl proton signals with the theoretical one demonstrates the possibilities of this method for the synthesis of a polymer with the given molecular weight.

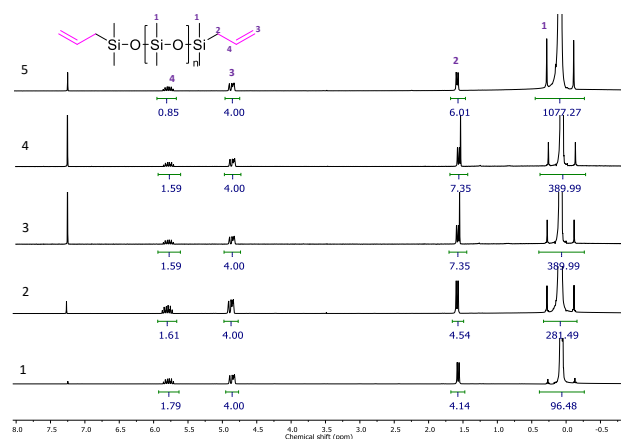


Figure 1. ¹H NMR spectra of the resulting polymers.

The yields of the siloxane products ranged from 90 to 98%, while the content of the high-molecular polymer according to the GPC data was about 87%.

Table 1. Molecular-weight characteristics of the resulting polymers

Polymer	Calc. MW	MW (NMR)	M_n	M_w	M_w/M_n
1	1000	1350	1480	2210	1.50
2	3000	3430	4100	7100	1.71
3	5000	4770	6100	10000	1.60
4	8000	7140	9200	16100	1.75
5	12000	10480	12300	21600	1.76

Experimental section

General remarks

All the reagents were used as received. Octamethylcyclotetrasiloxane (D4) was purchased from ABCR. Tetramethylammonium hydroxide (TMAH) was purchased from Acros (Belgium).

Analysis and general methodology

The ^1H NMR spectra were recorded on a Bruker Avance AV-300 spectrometer (300 MHz for ^1H).

The GPC analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD10A diode matrix detectors. The analytical separation was performed using a 7.8 mm \times 300 mm Phenomenex column (USA) filled with the Phenogel sorbent with the pore sizes of 15–500 Å.

Syntheses

General procedure for the synthesis of the allyl-PDMSn-allyl telechelics (1–5). A stirred mixture of 1,3-diallyl-1,1,3,3-tetramethyldisiloxane, octamethylcyclotetrasiloxane, and tetramethylammonium hydroxide (TMAH) was heated at 100 °C for 5 h. The conversion was monitored using GPC based on the depletion of the reaction mixture with D4. The catalyst was removed by the thermal decomposition at 150 °C for 1 h. The following evaporation of the volatiles ($p = 0.5$ bar, 100 °C) afforded the target product.

Conclusions

Based on our investigations, we proposed a simple method for obtaining PDMS telechelics with the allyl functional groups by the anionic opening of a siloxane ring. The resulting compounds are promising for the production of materials by the hydrosilylation reaction.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the detailed synthetic procedures, the GPC curves, and the NMR spectra of the resulting compounds. For ESI, see DOI: 10.32931/io2405a.

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